

## PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of

Mark Hernandez et al.

Serial No: 10/627,947

Filed: July 25, 2003

For: REMOVING METALS FROM SOLUTION  
USING METAL BINDING COMPOUNDS AND  
SORBENTS THEREFOR

Examiner: Ivars C. Clintins

Art Unit: 1724

Attorney Docket: MJ-1

Date: April 25, 2006

**CERTIFICATE OF ELECTRONIC TRANSFER** I hereby certify that this correspondence is being electronically transmitted to the United States Patent and Trademark Office on April 25, 2006.

Signed: 

Jay R Beyer

**DECLARATION UNDER 37 C.F.R. 1.132**

Commissioner of Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I Mark Hernandez, as a named inventor in U.S. Patent Application Serial No. 10/627,947 entitled REMOVING METALS FROM SOLUTION USING METAL BINDING COMPOUNDS AND SORBENTS THEREFOR (attorney docket no. MJ-1) hereby declare as follows.

Results from recent experimentation relating to the present invention are set forth below.

**EXPERIMENTAL SERIES****MATERIALS**

For purposes of a first set of experiments, an H-type carbon, Calgon MRX-P was selected for use. This carbon is readily commercially available and is well-known for industrial waste applications. In a first experiment, this carbon was saturated with 5g/L of methyl benzotriazole (MeBT). In particular, 34.7g of MRX-P was saturated to produce an effluent MeBT concentration of approximately 114 ppm.

For use in a second experiment, MRX-P was essentially converted to an L-type carbon or at least an L-like carbon by sustained oxidation. In this instance, 55g of MRX-P was oxidized by 20% HNO<sub>3</sub> for 8 hours. This L-type carbon was then saturated with methyl benzotriazole at 128mg MeBT/g of MRX-P.

Attorney Docket no. MJ-1

1 of 4

USSN 10/627,947

For use in a third experiment, 56.83g of MRX-P was oxidized, as was done for the second experiment, to produce L-type carbon. This carbon, however, was not exposed to MeBT.

The use of the same original MRX-P carbon in all three experiments is intended to eliminate variations in experimental results that might be caused on the basis of using different types of carbons.

## COLUMN TESTS

A first column experiment was carried out for the MeBT saturated MRX-P carbon using 75g carbon packed into a column with the volume of the carbon column being 10 ml. Contaminated solutions for use in this first set of experiments was obtained as an actual manufacturing by-product from a local printed circuit board manufacturer. This first experiment was conducted using a 50ppm Cu solution, prepared by diluting with deionized water and buffered to pH 3.5 using 1.5mM chloroacetic acid to adjust (i.e., further lower) the pH. The solution did not contain any level of appreciable competing ions such as magnesium and calcium. The solution was pumped through the column by a peristaltic pump at a hydraulic retention of 40 minutes. Samples were taken from the effluent periodically to measure the Cu concentration and the corresponding volume of Cu solution passed through was recorded. Results indicate that 0.00632g of Cu were removed per gram of MRX-P.

A second column experiment was carried out for the MeBT saturated L-type MRX-P carbon using 75g carbon packed into a column with the volume of the carbon column being 10 ml. This experiment was conducted using a different solution that was also obtained from the printed circuit board manufacturer and diluted with deionized water. This solution, in this case, contained 100ppm Cu, 400ppm Ca and 120ppm Mg buffered to pH 3.6 using 1.5mM chloroacetic acid such that a relatively large number of competing ions were present in solution for purposes of testing for metal selectivity. The solution was pumped through the column by a peristaltic pump at a hydraulic retention of 40 minutes. Samples were taken from the effluent periodically to measure the Cu concentration and the corresponding volume of Cu solution passed through was recorded. Results indicate that 0.014g of Cu was removed per gram of MRX-P.

A third column experiment was carried out for the L-type MRX-P carbon that was not exposed to the MeBT using 75g carbon packed into a column with the volume of the carbon being 10 ml. This experiment was conducted using the same stock solution that was used in the second column experiment containing 100ppm Cu, 400ppm Ca and 120ppm Mg buffered to pH 3.6 using 1.5mM chloroacetic acid. The solution was pumped through the column by a peristaltic pump at a hydraulic retention of 40 minutes. Samples were taken from the effluent periodically to measure the Cu concentration and the corresponding volume of Cu solution passed through was recorded. Results indicate that 0.0116g of Cu was removed per g of MRX-P.

## DISCUSSION AND COMPARISON OF EXPERIMENTAL RESULTS

In comparing the results of the experiments, more than twice as much copper was removed in the second experiment, as compared with the results of the first experiment. This result was found to be somewhat astonishing when it is remembered that the contaminated solution of the second experiment included a relatively large amount of

competing ions including magnesium ions and calcium ions (common components of water hardness). The amount of metal that was removed in the first experiment would necessarily decrease even further if the solution from the second experiment had been employed due to the presence of competing ions. The second experiment demonstrates not only what is believed to be a remarkably improved and unexpected level of metal removal capability, but a large and unexpected enhancement of selectivity for the contaminant metal in the presence of competing ions that are commonly found in industrial waste streams. The reason for this large improvement is related to a discovery that we have made with regard to the sorptive interactions of heterocyclic metal coordinating compounds with L-type carbon, as compared to H-type carbon, as will be further discussed below.

In comparing the results of the second and third experiments, remarkably, the L-type carbon that was saturated with MeBT removed 20.6% more copper than was removed by the L-type carbon alone. It is believed that this difference is attributable to the interactions of the heterocyclic metal coordinating compound with the L-type carbon, which to enhanced selectivity for the contaminant metal, in the presence of significantly higher concentrations of common competing ions (water hardness), over and above the selectivity and sorptive capacity that is provided by the L-type carbon alone. This is an important distinction, particularly when one considers that the removal of an additional 20% of toxic metal can be highly beneficial in preventing adverse consequences that could be caused by allowing this metal to remain in an environmental pollutant.

One reason for the dramatic improvements that have been attained using L-type carbon is attributed to the discovery that the conglomerate of interactions of L-type carbon with the heterocyclic metal coordinating compound in comparison with those realized by H-type carbon.

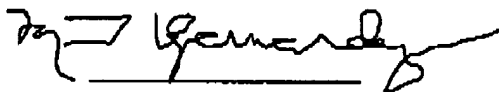
#### GENERAL DISCUSSION OF RESULTS

The experiments above clearly demonstrate that L-type carbon in combination with the heterocyclic metal coordinating compound provides for a greatly enhanced rate of target metal removal at depressed pH levels even in the presence of common competing, non-target ions (hardness) that were several times the concentration of the target (i.e. Copper). Thus, for a given value of pH, because of the conglomerate of interactions occurring between the L- carbon, the heterocyclic metal coordinating compound and the target metal itself, there is more net metal coordinating capacity available to sequester the metal from solution. This benefit is better optimized where the heterocyclic metal coordinating compound is interacting with L-type carbon. In this regard, the use of the L-type carbon in combination with the heterocyclic metal coordinating compound provided a 20% improvement over the use of the L-type carbon alone for direct sorption of the metal; and nearly 100% improvement of the removal capacity of H-type carbon in combination with the same heterocyclic metal coordinating compound that was not challenged by water hardness. It is noted that a paper, the pertinence of which only recently came to my attention, entitled "The Influence of Active Carbon Oxidation on the Preferential Removal of Heavy Metals" by Strelko, et al., submitted in an Information Disclosure Statement which accompanies this response, describes the use of L-type carbon for direct sorption of the metal, but fails to recognize, even over a number of ensuing years, that any benefit could be achieved by the combination of L-type carbon with a heterocyclic metal coordinating compound, as will be further discussed below.

It is thought that the main reason for the improved removal ability of L-type carbon at low pH, through direct sorption of the metal as compared to direct sorption by H-type carbon, resides in the L-type carbon exhibiting lower pH values at the point of zero charge (PZC: the surface charge of the carbon surface is zero at that pH value) when compared to the pH at the PZC for H-type carbon. The surface of active carbons immersed in aqueous solutions can be either positively or negatively charged, dependent upon the solution pH. House and Shergold (1984), well before the Strelko paper, found that the metal sorption capacity of active carbons depends on the pH value at the PZC. These researchers observed an abrupt reduction in metal sorption as the external solution pH approached this value. The removal of cations is favored at pH values above PZC and is inhibited for anions. Acidic functional groups on the surface of carbons act as ion-exchange sites for metals. The solution pH must be above or near the pK values of functional groups for cations to be adsorbed by the carbon.

Even with the foregoing information in hand, we are the first to discover optimized sorption of a heterocyclic metal coordinating compound to L-type carbon, which could be based on zero point charge. This is demonstrated by two more recent papers that were published by Strelko in 2004 and 2005, subsequent to my patent application, and which have been provided as Exhibit A and Exhibit B. I find no mention of the use of a heterocyclic metal coordinating compound in combination with L-type carbon in these papers. Clearly, the earlier, 2001 Strelko paper also failed to recognize the remarkable results that I have obtained using the heterocyclic metal coordinating compound in combination with L-type carbon.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.



Mark Hernandez

April 21, 2006